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(54) Title of Invention A tetrafluoroethylene-hexafluoropropene copolymer and
fluoroelastomer composition

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(56) References: Tokko [Japan examined patent application] S38-26570 (JP, B1)

(57) **Scope of Patent Claims**

1 A tetrafluoroethylene-hexafluoropropene copolymer and fluoroelastomer composition characterized in that 0.05-10 weight percent of a fluoroelastomer is uniformly compounded into 99.95-90 weight percent of a tetrafluoroethylene-hexafluoropropene copolymer.

Detailed Description of the Invention

The present invention concerns a tetrafluoroethylene-hexafluoropropene copolymer and fluoroelastomer composition.

Because copolymers of tetrafluoroethylene (TFE, below) and hexafluoropropene (HFP, below) have heat resistance, chemical resistance and electrical properties rivaling those of polytetrafluoroethylene (PTFE, below) and furthermore have melt flow properties not found in PTFE, melt processing [of these copolymers] by any method, such as compression molding, extrusion molding and injection molding, is possible, and they are used in a wide variety of applications.

In general, for TFE/HFP copolymers used in extrusion molding, injection molding and the like, a relative melt viscosity, which will be defined later, in the range of 10^4 - 10^5 poise is required from the standpoint of moldability.

However, in TFE/HFP copolymers with relative melt viscosity of 10^5 poise or less, stress cracks occur relatively easily at temperatures of 180°C or higher, and because of that, their range of use is limited. When their relative melt viscosity reaches 5×10^5 poise, their stress crack properties improve, and stress cracks do not occur up to the vicinity of the melting point, but the increase in relative melt viscosity means a reduction in moldability and is undesirable.

There are 2 conceivable [types of] methods for ameliorating disadvantages of this kind inherent in TFE/HFP copolymers: methods by means of polymerization, in which other monomers are copolymerized [with them], denaturizing agents are added, or polymerization conditions are changed during their manufacture, and methods by means of blending other substances [with them]; and the present invention belongs in the latter of these categories.

That is, the present invention ameliorates the aforementioned heat stress cracking of TFE/HFP copolymers without sacrificing their moldability, providing a TFE/HFP copolymer composition with excellent resistance to heat stress cracks, and this objective is achieved by uniformly compounding 0.05-10 weight percent of a fluoroelastomer into 99.95-90 weight percent of a tetrafluoroethylene-hexafluoropropene copolymer.

A TFE/HFP copolymer in the present invention is one that is composed mainly of TFE and HFP, that has an HFP content, to be defined later, of 5-20 weight percent, and it may include small amounts of a third component, denaturing agent[s], and the like.

In addition, examples of the fluoroelastomer in the present invention include HFP-vinylidene fluoride copolymer, TFE-vinylidene fluoride-HFP terpolymer, TFE-propylene copolymer, TFE-chlorovinyl ether copolymer, TFE-ethylene-propylene terpolymer, ethylene-HFP copolymer, TFE-ethylene-HFP terpolymer, TFE-ethylene-hexafluoroacetone terpolymer and TFE-hexafluoroacetone copolymer, and one or a mixture of 2 or more of these can be used.

Any mixing method, wet or dry, using, for example, a mixer, mixing rolls, a kneader, a ball mill, a Banbury mixer or a blender, can be employed as the method for compounding the fluoroelastomer into the TFE/HFP copolymer. In general, it is preferable to prepare the fluoroelastomer as a water-based dispersion, and wet-mix it with the TFE/HFP copolymer. In addition, the fluoroelastomer may be added to and/or during the polymerization reaction as the TFE/HFP copolymer is manufactured, and this method has absolutely no adverse effect on the polymerization reaction or the resulting product.

In order to obtain the aforementioned effect of the present invention, it is necessary that the fluoroelastomer be uniformly mixed (blended) at the molecular level into the TFE/HFP copolymer in the state in which it forms the final molded article, and for this purpose, any of the aforementioned mixing means is no more than an incomplete and rough mixing, and a final melt mixing must be carried out; but melt mixing of this kind can be attained spontaneously by means of pelletizing during production of manufactured articles. In addition, in cases in which piping is extruded directly to make final manufactured articles without going through a pelletizing process, the objective of uniform mixing can be attained by means of that melt extrusion.

According to the present invention, by compounding 0.05-10 weight percent of a fluoroelastomer into 99.95-90 weight percent of a tetrafluoroethylene-hexafluoropropene

copolymer, more preferably 0.1-5.0 weight percent of a fluoroelastomer into 99.9-95.0 weight percent of a tetrafluoroethylene-hexafluoropropene copolymer, heat stress cracking resistance can be improved with almost no loss of the special characteristics of TFE/HFP copolymers. No effect is found if the amount of fluoroelastomer added is small, and if the amount added is too large, discoloration, reduction in mechanical strength and the like occur, and this is undesirable.

If the elastomer added is a hydrocarbon-based elastomer, defects such as insufficient heat resistance occur. Furthermore, any other fluororesins, such as, for example, polyfluorovinylidene, polytetrafluoroethylene, polytetrafluoroethylene wax, tetrafluoroethylene-fluorovinyl ether copolymer have no effect.

Working examples, comparison examples and test examples are presented below to explain the working embodiments of the present invention. In the working examples and comparison examples, "parts" means those according to a weight standard, unless otherwise stated. In addition, HFP content (weight percent) is shown as a numerical value that is 3.2 times the result of dividing the absorbance by infrared absorption spectrum at wave number 980 cm^{-1} of a film approximately $40\text{ }\mu$ thick by its absorbance at wave number 2350 cm^{-1} . Furthermore, relative melt viscosity was determined using a Koka type flow tester, and was obtained by packing the polymer into a cylinder with an inner diameter of 9.5 mm, and after first holding it at a temperature of 380°C for 5 minutes, extruding it at the same temperature through an orifice with an inner diameter of 2.1 mm and a length of 8 mm under a piston load of 5 kg, and dividing 53150 by the extrusion speed (cc/min) at this time.

Working Example 1

100 parts of a powdered TFE/HFP copolymer, with a relative melt viscosity of 8×10^4 poise and an HFE content of 12.2%, and 500 parts of ion exchange water are vigorously agitated in a tabletop mixer; 10 parts of a water-based dispersion containing 10% of TFE-propylene copolymer elastomer (molar ratio of polymer components TFE/propylene = 1) are added; and after agitating this for 30 minutes, 5 parts of 20% nitric acid is added as a coagulant. After further agitation for 30 minutes, it is filtered, thoroughly washed with ion exchange water, and dried for 24 hours at a temperature of 120°C . In the above filtering and washing operations and so on, almost no escaped grains of TFE-propylene elastomer were observed. The polymer pre-mixed in this way is extruded at a temperature of 330°C by means of a screw extruder with a cylinder length of 2200 mm, a diameter of 15 mm, a dispensing orifice diameter of 2 mm and a dispensing orifice length of 10 mm, and this extruded material is once more extruded by the same method to pelletize it, to obtain a blended polymer. The relative melt viscosity of this polymer was 7.6×10^4 poise, and its HFP content was 12.2%.

Working Example 2

The operations were carried out in the same way as in Working Example 1, except that 5 parts of a water-based dispersion containing 22% of TFE-HFP-vinylidene fluoride elastomer having a composition of 20 mol percent TFE, 31 percent HFP and 49 percent vinylidene fluoride were used as the added elastomer, to obtain a blended polymer with a relative melt viscosity of 7.4×10^4 poise and an HFP content of 12.2%.

Working Example 3

1000 parts of deoxygenated and demineralized water were put into a jacketed SUS-32 agitation-type autoclave with a capacity of 3000 parts water, 20 parts of the TFE-propylene

elastomer water-based dispersion of Working Example 1 were added, and the interior space was thoroughly replaced with pure nitrogen gas; then, 600 parts of HFP and 110 parts of TFE were added under pressure. The temperature in the tank was maintained at 20°C, and, while agitating, 2 parts of di(omegahydrodecafluoroheptanoyl)peroxide were added as a polymerization initiator and 14 parts methyl alcohol as a molecular weight adjusting agent. The reaction was initiated immediately, and TFE was consecutively supplied as the reaction proceeded. After the reaction continued in this way for 24 hours, unreacted monomers were released, and after 3 parts of 20% nitric acid were added, the polymer was retrieved. After the polymer was thoroughly washed, it was dried for 24 hours at a temperature of 120°C to obtain 135 parts of white powdered blended polymer. The relative melt viscosity of this polymer was 7.2×10^4 poise, and its TFP¹ content was 12.2%.

Working Example 4

The operations were carried out in the same way as in Working Example 3, except that 5 parts of the TFE-vinylidene fluoride-HFP elastomer water-based dispersion of Working Example 2 were used as the added elastomer, to obtain 143 parts of blended polymer with a relative melt viscosity of 8×10^4 poise and an HFP content of 12.0%.

Comparison Example 1

The operations were carried out in the same way as in Working Example 3, except that no elastomer was added, to obtain 140 parts of polymer with a relative melt viscosity of 8×10^4 poise and an HFP content of 12.3%.

Comparison Example 2

The operations were carried out in the same way as in Working Example 3, except that no elastomer was added, the [amount of] methyl alcohol was 10 parts, and the polymerization time was 30 hours, to obtain 165 parts of polymer with a relative melt viscosity of 1.5×10^5 poise and an HFP content of 12.2%.

Comparison Example 3

The operations were carried out in the same way as in Working Example 1, except that 120 parts of the TFE-vinylidene fluoride-HFP elastomer water-based dispersion of Working Example 2 were used as the added elastomer, to obtain a blended polymer with a relative melt viscosity of 3.2×10^4 poise.

Comparison Example 4

The operations were carried out in the same way as in Working Example 1, except for using 0.3 parts of the water-based dispersion of added elastomer, to obtain a blended polymer with a relative melt viscosity of 7.8×10^4 poise and an HFP content of 12.2%.

Test Example

For the polymers of the working examples and the comparison examples, heat stress crack resistance was measured by the method below.

First, a 24 g sample is packed into a cylindrical metal mold with a diameter of 80 mm, and this is put into an electric oven and held at a temperature of 330°C for 25 minutes. After

¹ Typo in original?

subsequently holding it for 1 minute at the same temperature under 60 kg/cm² pressure, it is water-cooled to obtain a sheet with a thickness of 2.3-2.4 mm. After this sheet is heated by the electric oven at 240°C for 20 hours, rectangular test samples 39 mm long and 13 mm wide are taken, and cuts made 11 mm long and 0.5 mm deep with a razor blade in the center, in the direction of the long side. The samples are subsequently bent and set in an ASTM D1693-70 standard sample holder, with the surface with the above cut on the outside, and placed in 180°C and 215°C electric ovens with viewing windows. The time until cracks occurred in half of 20 measuring test samples was measured and taken as the heat stress crack resistance.

The results are shown in Table 1. From these results, it can be understood that, compared with Comparison Example 1, which contained no fluoroelastomer, and Comparison Example 2, which had a high relative melt viscosity, cracks occurred with difficulty in all the working examples, and that heat stress crack resistance values were greatly increased by means of the addition of a small amount of fluoroelastomer.

Table 1

	Relative melt viscosity (poise)	Yield strength* (kg/cm ²)	Elongation (%)	Stress crack resistance		Appearance of test sample after testing
				180°C	215°C	
Working Example 1	7.6 x 10 ⁴	130	350	>20 h	45 min	No discoloration
Working Example 2	7.4 x 10 ⁴	131	—	>20 h	38 min	Slight discoloration
Working Example 3	7.2 x 10 ⁴	134	—	>20 h	38 min	No discoloration
Working Example 4	8.0 x 10 ⁴	131	345	>20 h	40 min	Slight discoloration
Comparison Example 1	8 x 10 ⁴	142	280	1 h	<5 min	No discoloration
Comparison Example 2	1.5 x 10 ⁵	141	—	>20 h	15 min	No discoloration
Comparison Example 3	3.2 x 10 ⁴	95	200	>20 h	—	Brown
Comparison Example 4	7.8 x 10 ⁴	135	—	1 h	<5 min	No discoloration

* Measured according to the method described in ASTM D 638.